



TITLE:

Oxidation Involved in Organometallic Reactions (Commemoration Issue Dedicated to Professor Minoru Ohno On the Occasion of his Retirement)

AUTHOR(S):

Ichikawa, Katsuhiko; Uemura, Sakae

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Oxidation Involved in Organometallic Reactions

Katsuhiko ICHIKAWA* and Sakae UEMURA**

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Results, obtained on the oxidation involved in organometallic reactions, have been classified into SN1 and SN2 type, oxidative substitution in aromatics, oxidative coupling and oxidative addition. Major interests are in the reactions of Hg, Tl, Cu and Pd compounds. Related results reported in the literature are also reviewed briefly.

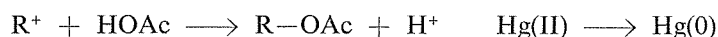
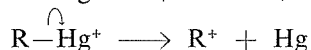
Organometallic compounds involving polyvalent heavy metal atoms show many other interesting properties than those of carbanion chemistry which is the major interests in organometallics such as alkali metal and magnesium compounds. Present paper reviews our results on the oxidation involved in organo-mercury, -thallium, -copper and -palladium compounds.

Related results reported in the literature are also reviewed briefly.

As an organic reaction, the present oxidation can be classified into 1. SN1 type, 2. SN2 type, 3. oxidative substitution in aromatics, 4. oxidative coupling, and 5. oxidative addition.

1. SN1 Type

Alkyl- and aralkyl-mercuric salts, when dissolved in acetic acid containing strong acids such as perchloric acid and boron trifluoride, give alkyl and aralkyl acetate.¹⁾



Rates of reaction change remarkably by the changes in X, the structure of R and acidity of the reaction medium. This type of reaction is in sharp contrast to the usual one of organometallics in which R is splitted with proton to give RH.



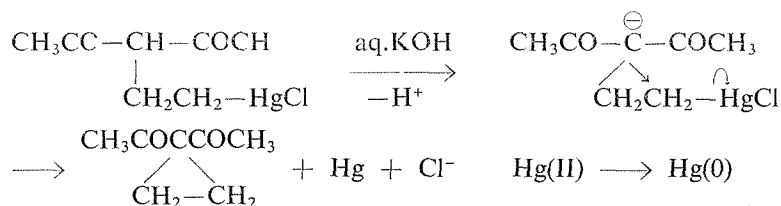
The driving force of this unusual reaction is the oxidizing power of mercury(II).

2. SN2 Type

3,3-Diacetylpropylmercuric chloride, which can be obtained by the reaction of oxymercurial from ethylene with acetylacetone, gives 1,1-diacetylcyclopropane upon treating with aqueous potassium hydroxide at room temperature.²⁾

* 市川 克彦: Laboratory of Petroleum Chemistry, This Institute, and Department of Hydrocarbon Chemistry, Kyoto University, Yoshida, Kyoto.

** 植村 栄: Laboratory of Petroleum Chemistry, This Institute.



According to the usual classification, this type of reaction belongs to S_{Ni} or γ -elimination. The driving force is the oxidizing power of mercury(II) assisted with nucleophilic attack of carbanion.

3. Oxidative Substitution in Aromatics

Aromatic mercuriation is well known as a typical electrophilic aromatic substitution in which the valency of Hg(II) remains unchanged throughout the reaction.³⁾ In the case of oxynitration of aromatics with nitric acid in the presence of mercury salt, however, it seems likely that the catalytic role of mercury involves oxidation-reduction.⁴⁾

This type of aromatic oxidation with metallic salts might be a possible method of preparation of phenols from aromatic hydrocarbons.

Along this line, several experiments have been done. Palladium(II) salts react with aromatic hydrocarbons to give three types of products, phenol derivatives, aromatic coupling products and oxidation products of side chains. Product distributions vary remarkably by changing gegen ions of Pd(II) .

For example, the main product of the reaction of benzene with $\text{Pd(NO}_3)_2$ in acetic acid at 90° is phenyl acetate, while biphenyl is the only product with $\text{PdSO}_4 \cdot 2\text{H}_2\text{O}$. Table I shows examples of the product distributions with various Pd(II) salts.⁵⁾

Table I. Products of the Reaction of Aromatics with Pd(II) Salts in Acetic Acid ($95-100^\circ\text{C}$, 4hr)

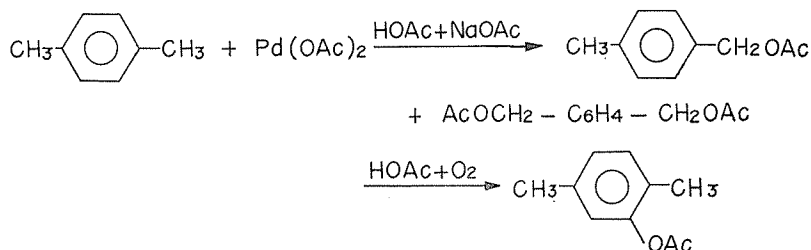
$\text{C}_6\text{H}_6 + \text{Pd(NO}_3)_2$	\longrightarrow	$\text{C}_6\text{H}_5\text{OAc}$	$+ \text{C}_6\text{H}_5\text{NO}_2$	$+ \text{C}_6\text{H}_5\text{C}_6\text{H}_5$
		39	14	4.5
$+ \text{Pd(NO}_3)_2 + \text{H}_2\text{O}(20\%)$	\longrightarrow	12	trace	69
$+ \text{PdSO}_4 \cdot 2\text{H}_2\text{O}$	\longrightarrow	trace	—	51
$+ \text{PdCl}_2$	\longrightarrow	—	—	trace
$+ \text{PdCl}_2 + \text{NaOAc}$	\longrightarrow	trace	—	59
$+ \text{Pd(OAc)}_2$	\longrightarrow	6	—	24
$+ \text{Pd(OAc)}_2 + \text{HNO}_3$	\longrightarrow	34	18	trace
$+ \text{Pd(OAc)}_2 + \text{NaOAc}$	\longrightarrow	1	—	15
HOAc				
$\text{MeC}_6\text{H}_5 + \text{Pd(NO}_3)_2$	$\xrightarrow{90^\circ}$	$o\text{-MeC}_6\text{H}_4\text{OAc}$	$+ m,p\text{-MeC}_6\text{H}_4\text{OAc}$	$+ \text{C}_6\text{H}_5\text{CHO}$
		11	24	trace
		$+ o\text{-MeC}_6\text{H}_4\text{NO}_2$	$+ m\text{-MeC}_6\text{H}_4\text{NO}_2$	$+ p\text{-MeC}_6\text{H}_4\text{NO}_2$
		trace	11	8

Recent report⁶⁾ revealed that oxygen plays an important role in determining product distribution (Table II). It is assumed that the reaction proceeds through oxypalladation and dehydropalladation. The troubles in the experiments with Pd(OAc)_2 , however, are poor reproducibilities and difficulties in the preparation of

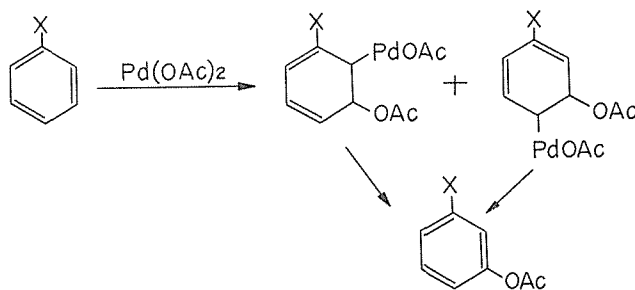
Oxidation Involved in Organometallic Reactions

pure $\text{Pd}(\text{OAc})_2$. Traces of impurities might change the product distributions completely. Our results did not agree with those mentioned above, and further experiments are required for the determination of detailed mechanism.

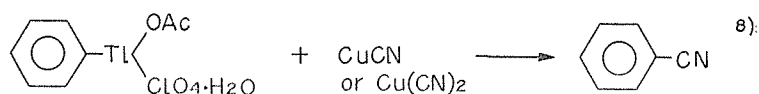
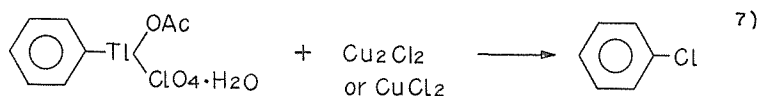
Table II. Oxidation of Aromatics with $\text{Pd}(\text{OAc})_2$



	$\text{Pd}(\text{OAc})_2$			Anodic oxid.		
	<i>o</i> -	<i>m</i> -	<i>p</i> -	<i>o</i> -	<i>m</i> -	<i>p</i> -
<i>t</i> -Butylbenzene	—	95	5	35	22	43
Anisole	1	97	2	67	4	29
Biphenyl	2	98	—	31	1	68
Chlorobenzene	3	88	9	37	5	58
Bromobenzene	5	81	14	30	3	67
Iodobenzene	25	69	6	18	4	78
Naphthalene	50	50	—	96	4	—

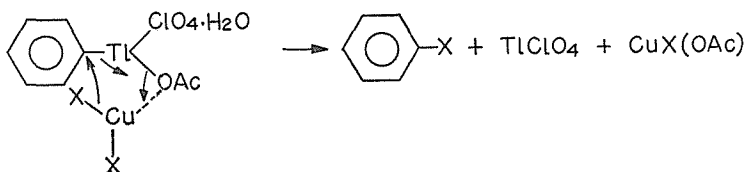


Several examples in oxidative substitution of aromatic organometallics have been obtained in the case of thallium(III) compounds.

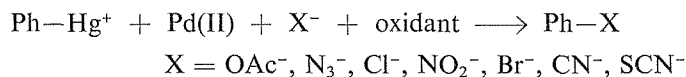


This type of reaction does not proceed in the presence of alkali metal salts, although

it is reported that irradiation of aqueous solution of $\text{PhTl}(\text{OCOCF}_3)_2$ containing potassium cyanide gives benzonitrile.⁹⁾ Copper salts are required and both cuprous and cupric salts react similarly. The results are similar to those of decomposition of diaryliodonium salts with cuprous chloride¹⁰⁾ and Sandmeyer reaction of aromatic diazonium ions.¹¹⁾ Tentative mechanism (SNC; Substitution, Nucleophilic, Co-ordination) is assumed as follows.

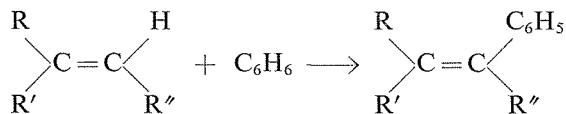


The same type of reaction with mercury compounds was reported recently.¹²⁾

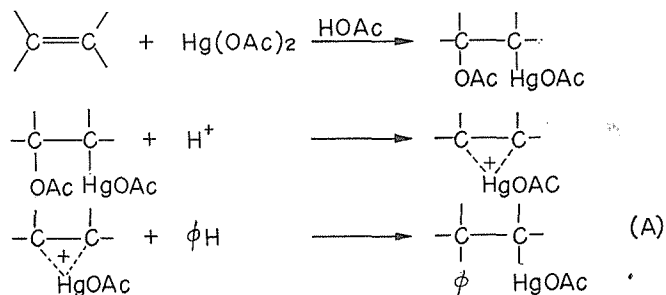


The role of oxidant in this reaction and the relationship to our reaction with thallium(III) compounds are not yet clear.

Moritani and his co-workers reported that the olefinic hydrogen can be substituted stereospecifically with aromatics by the reaction with palladous chloride in acetic acid.¹³⁾



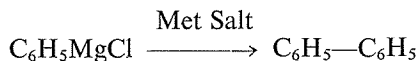
For the mechanistic consideration, the following reaction of oxymercurials of olefins¹⁾ might be suggestive.



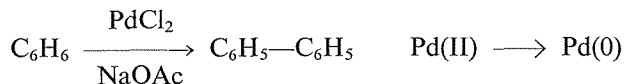
In the case of mercury, A is stable and can be isolated in good yields. If an analogy could be applicable to the case of palladium, the corresponding intermediate (A) would be unstable and undergo dehydropalladation. Assuming *trans* oxypalladation and *cis* dehydropalladation, the stereochemistry could be explained.

4. Oxidative Coupling

It is well known that Grignard reagents give coupling products through radical mechanism in the presence of transition metal salts.¹⁴⁾



Recently direct coupling of aromatic hydrocarbons in the presence of Pd(II) salt have been reported.¹⁵⁾

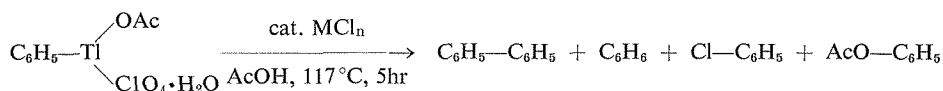


The relationship between the mechanisms of the two types of coupling reaction appears to be important to clarify the chemistry of organopalladium compound. It is pointed out that Pd(II) salt reacts with aromatics as an electrophilic reagent.¹⁶⁾ If this is the case, the coupling might be the results of the reaction of arylpalladium compounds. In order to make this problem clear, and to generalize it further to other cases of various metals, the reaction of aromatic thallium compounds in the presence of catalytic amounts of various metal halides has been studied, since the thallium compounds can be prepared easily by the reaction of thallic acetate with aromatics under the conditions which are similar to those of direct coupling with Pd(II) salt.¹⁷⁾

Phenylthallic acetate perchlorate $\text{C}_6\text{H}_5\text{Tl}(\text{OAc})(\text{ClO}_4) \cdot \text{H}_2\text{O}$ was subjected to the reaction with various metallic salts in refluxing acetic acid for 5 hrs. Four kinds of product, biphenyl, benzene, chlorobenzene and phenyl acetate were obtained. Benzene and chlorobenzene, and phenyl acetate were the products of dethallation with acid and the oxidative substitution mentioned earlier respectively.

Yields of biphenyl changed remarkably by the change of metal salts. The results are reported in Table III.¹⁸⁾

Table III. Yields of Coupling Product by the Reaction of $\text{C}_6\text{H}_5\text{Tl}(\text{OAc})(\text{ClO}_4) \cdot \text{H}_2\text{O}$ with Various Metal Salts.



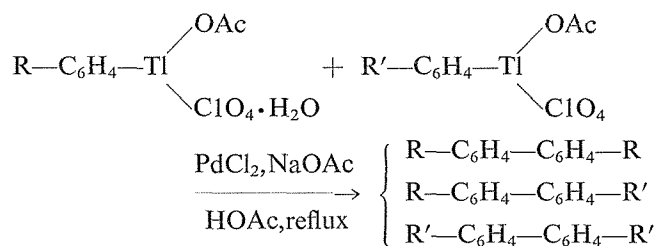
$\text{C}_6\text{H}_5\text{—C}_6\text{H}_5$ Yield	MCl_n
Below 30%	Ag(I) Au(III) Zn(II) Cd(II) Tl(I) Sn(II,IV) <u>Ti(IV)</u> Sb(III,V) Cr(III) Mn(II) Re(V) <u>Fe(III)</u> <u>Ru(III)</u> Co(II) Rh(III) Ni(II)
Above 30%	Pd(II) Pt(IV) Fe(II) Cu(II) Tl(III) Hg(II)

Only in the case of RuCl_3 (added with NaOAc), phenyl acetate was obtained in

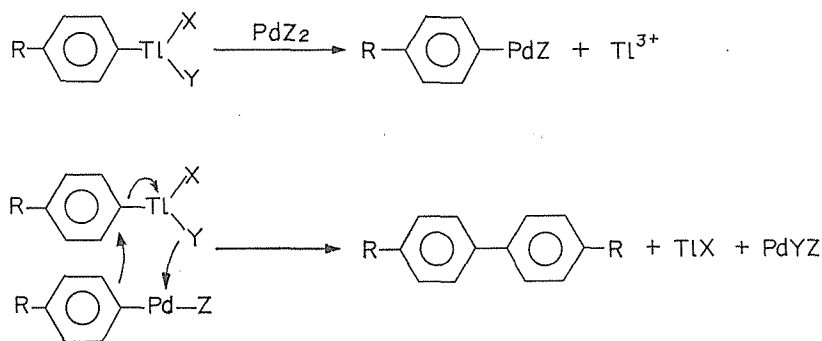
11% yield together with almost the same yield of biphenyl. In the cases of ferrous chloride (hydrated), anhydrous cupric chloride and thallic chloride, the yields were not reproducible and changed in the range between 5–95%, suggesting the radical mechanism.

With palladium chloride, however, radical mechanism appears to be inapplicable, since the addition of radical scavenger or the radical sources did not affect the product distribution nor the yields of biphenyl.

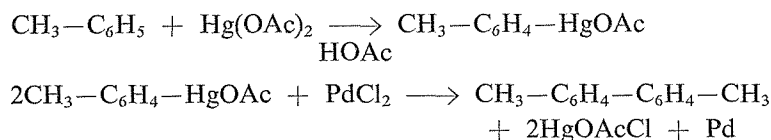
Mixtures of arylthallic salts gave cross coupling products.



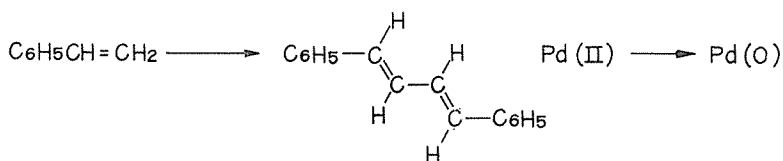
In the cases of phenyl- and tolyl-, and phenyl- and *o*-xylyl derivatives, the ratios of the yields of R–R, R–R' and R'–R' were about 1:2:1, *i.e.*, statistical values in both cases. The mixture of $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{Ti}(\text{OCOCF}_3)_2(\text{R})$ and $\text{Cl} \cdot \text{C}_6\text{H}_4 \cdot \text{Ti}(\text{OCOCF}_3)_2(\text{R}')$ gave R–R, R–R', R'–R' in a ratio of 1:1.3:0.4, showing that the coupling is slower in the case of phenylthallic derivative substituted with negative group. Tentative mechanism was proposed as follows:



The same kind of coupling of phenylmercuric acetate (prepared *in situ*) with PdCl_2 was reported by Unger and Fouty.¹⁹⁾



In the reaction of styrene with Pd(II) salts in refluxing acetic acid, the formation of *trans-trans*-1,4-diphenylbutadiene was observed. This is the same type of oxidative coupling with olefin.²⁰⁾



5. Oxidative Addition

a. Oxymetallation

Metal salts react with olefins to form two types of organometallic compound, oxymetallation product and π -complex.²¹⁾ A number of oxymercurials have been prepared and well characterized.



R = H, alkyl or acyl

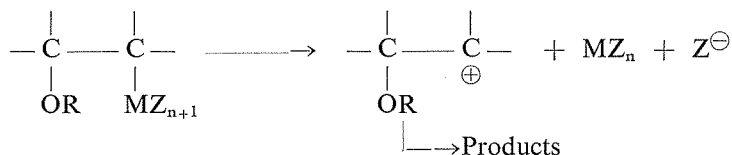
Usually, the addition proceeds very fast in *trans* form without side reaction at room temperature. Recent reports revealed that amines could be used as the solvent and oxymercuration could be extended further to solvomercuration.²¹⁾

Through oxythallation with thallic acetate, several oxythallation products have been isolated.²¹⁾ In contrast to the case of oxymercuration, where the products are very stable usually, those of oxythallation are rather unstable and not always easy to isolate.

With lead tetraacetate, no oxyplumbation product has been isolated yet, although some evidence for the formation of the same kind of product could be obtained in a special case.²¹⁾

It is well known that palladous chloride forms π -complexes with various olefins and whether oxypalladation occurs or not has been a subject of discussion. However, these are assumed as the intermediate of many reactions of π -complexes, and the relation between π -complex formation and oxypalladation appears to be important to understand the reaction of olefins with palladium salts.

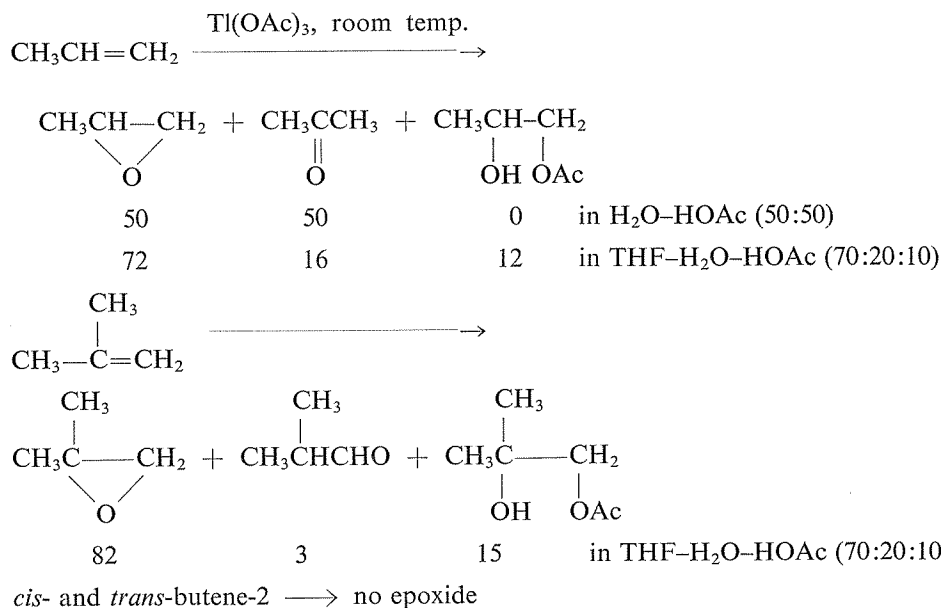
In general, oxidation of olefins with Hg(II), Tl(III) and Pb(IV), including those of enols, appears to proceed through oxymetallation.



Since the formation and reaction of oxymetallation products have been summarized in several reviews,²¹⁾ only recent results are described here.

Recently, it was reported that epoxidation of propylene and isobutylene proceeds

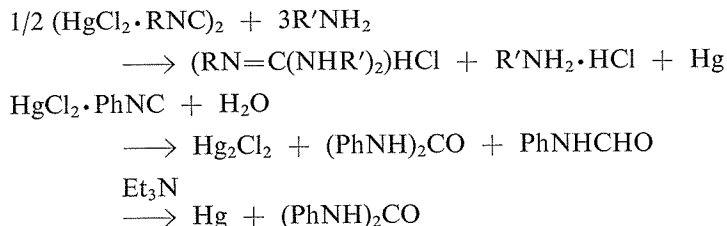
by the oxidation of thallic acetate in H_2O – HOAc or THF – H_2O – HOAc .²²⁾



This type of reaction has never been observed in the case of oxymercurials, since they are much more stable. For the demercuration of oxymercurials, the presence of strong acid is required usually and the epoxide will react further to form glycols or carbonyl compounds even if it could be formed.

Although much work on oxymetallation reactions of olefins has been published, little is known of those with conjugated dienes. While only 1,2-addition was reported with mercuric acetate, 1,4-addition also has been observed with thallic and plumbic acetate.²³⁾ Both synthetic and mechanistic works are required in the field.

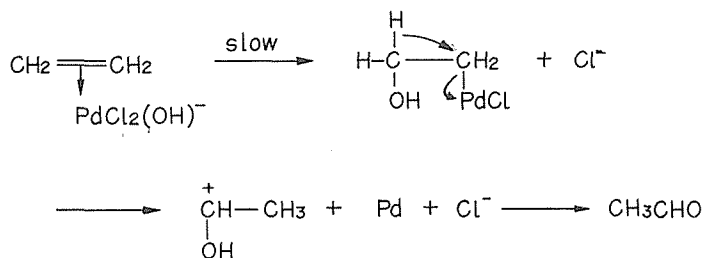
The formation of guanidine and urea derivative from isocyanate– HgCl_2 is reported recently.²⁴⁾ Although the mechanism was not discussed, the reaction could be through oxymercurials of $\text{N}\equiv\text{C}$ triple bond.



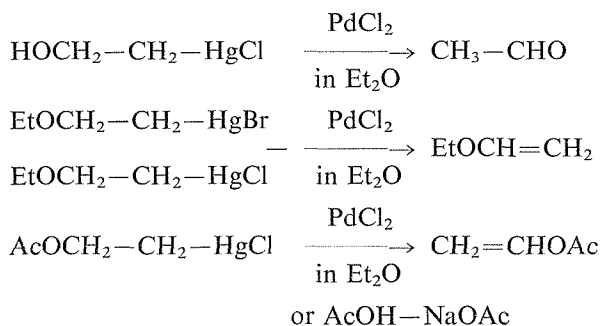
b. Reaction with Pd(II) Salt

As is mentioned above, oxypalladation product has not yet been isolated except in the case of some dienes. However, its formation has been assumed in various types of oxidation of olefin with $\text{Pd}(\text{II})$ salts. For example, even in the typical reaction of π -complex of ethylene to form acetaldehyde (Höchst-Wacker process), oxypalladation

product is assumed as an intermediate.



Direct oxypalladation of olefin has been often postulated in the case of palladous acetate oxidation. Conflicting conclusions on the same cyclohexene oxidation, however, have been reported recently.²⁵⁾ As a possible method of studying this problem is to analyze the reaction of palladium salt with oxythallium and oxymercury compounds, since the metal exchange is expected to form oxypalladium compound. It was reported that hydroxy-, ethoxy- and acetoxy-ethylmercuric salts react with palladium chloride in ether to give acetaldehyde, vinyl ethyl ether and vinyl acetate respectively.²⁶⁾

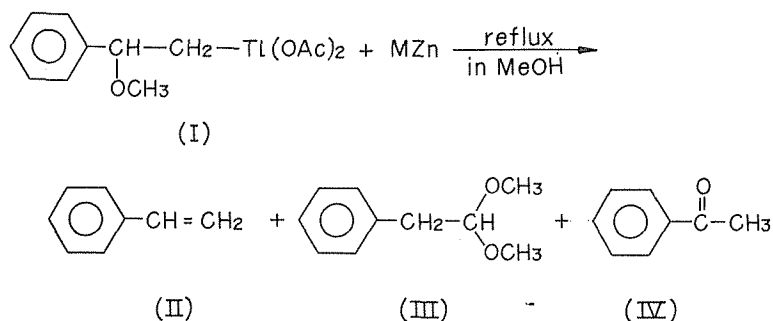


These products are the same as those obtained by the oxidation of ethylene with palladous chloride in water and with palladous acetate in acetic acid. The special feature of the results is that hydride shift occurred in hydroxy-ethylpalladium salt while dehydropalladation proceeded in ethoxy- and acetoxy-ethylpalladium salt.

Along the same line, oxythallium and oxymercury compound from styrene have been subjected to the reaction with palladium salt. In the absence of palladium salt, the oxythallium compound gave phenylacetaldehyde acetal upon refluxing in methanol solution. Addition of palladous chloride resulted in the formation of acetophenone ketal together with phenylacetaldehyde acetal. In the presence of sodium acetate, only ketal was formed. It appears that ketal has resulted from oxypalladium compounds which is formed by metal exchange of oxythallium compound, and the presence of sodium acetate accelerated the exchange. Typical results are presented in Table IV.²⁷⁾

The addition of boron trifluoride or cupric chloride increased the yield of acetal, but did not form ketal. The mechanism of acetal formation is believed to be as follows.

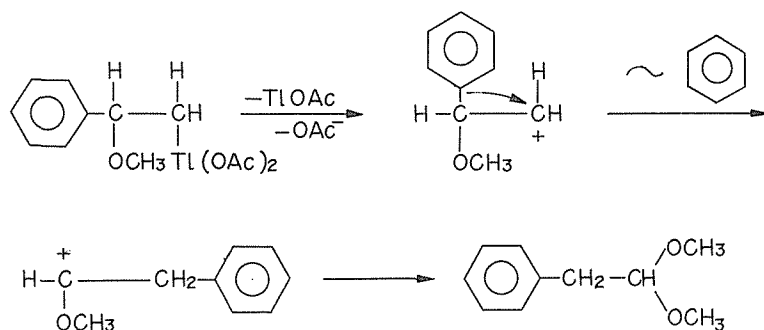
In the absence of Pd salt, the carbonium ion, resulted from dethallation, forms



I mmole	MZ _n , mmole	NaOAc mmole	Time hr	Products yield %		
				II	III	IV
10*1	—	—	5	0	37	0
10*1	PdCl ₂ , 10	—	5	0	38	47
5*2	PdCl ₂ , 5	10	0.17	0	0	87
5*2	CuCl ₂ , 5	—	5	13	62	0
5*2	BF ₃ , 5	—	5	0	92	0

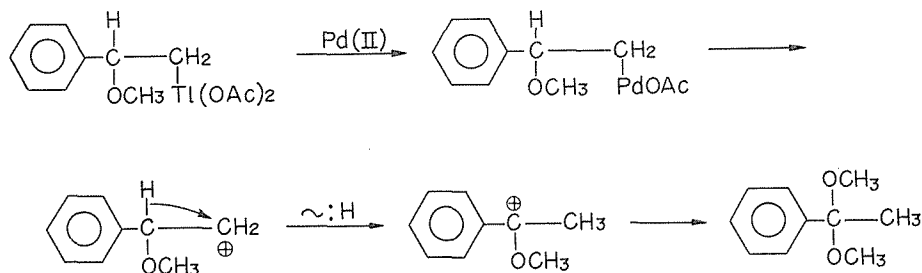
*2 MeOH 25ml

the acetal through phenyl migration.



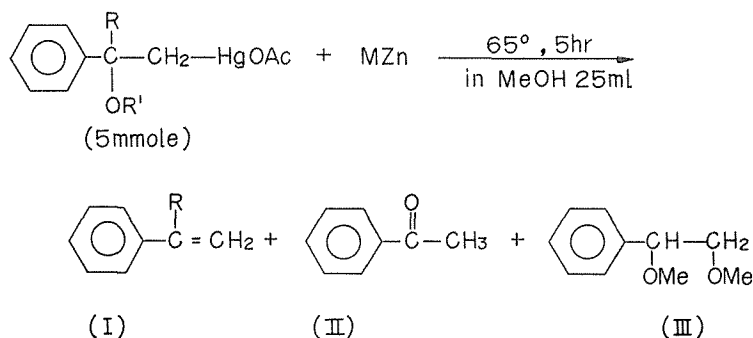
In the presence of Pd salt, the metal exchange forms oxypalladation product. Dehydro-palladation which is assumed in palladous acetate oxidation should form α -phenyl-vinyl methyl ether, which in turn might form acetophenone ketal through addition of methanol. If this is the case, acetophenone should contain deuterium when the reaction is carried out in methanol-O-d. Since no deuterium incorporation was observed, this reaction scheme is not applicable. If the hydride shift can be assumed as in the case of ethylene oxidation (p 233), the ketal formation can be explained as mentioned above.

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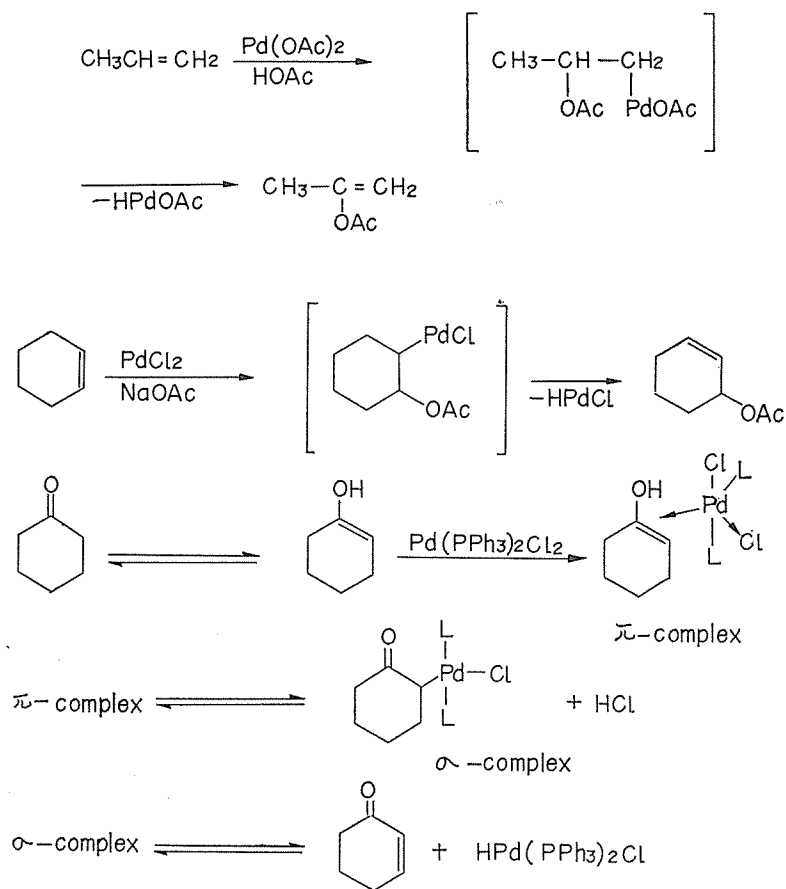
In general, however, phenyl migration is much more easy than hydrogen migration usually. The above mechanism, therefore, must be oversimplified one, and the detailed mechanism requires further investigation in connection with dehydropalladation which is assumed in many cases. Using oxymercury compounds, the same kind of result has been obtained (Table V).

Table V. Effects of Additives on the Product Distributions on the Reaction of Oxymercury Compound of Styrene



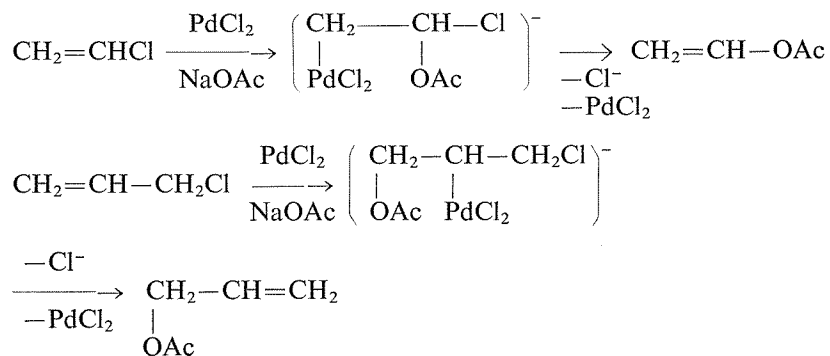
R	R'	MZn, mmole	NaOAc mmole	Products yield %			Note
				I	II	III	
H	CH ₃	PdCl ₂ , 5	10	0	89	0	<i>in situ</i>
H	CH ₃	BF ₃	—	0	0	47	
H	CH ₃ CO	PdCl ₂ , 5	10	13	68	0	
CH ₃	CH ₃	PdCl ₂ , 5	10	63	0	0	<i>in situ</i>
CH ₃	CH ₃	BF ₃ , 5	—	38	0	0	<i>in situ</i>

Direct oxidation of olefins with palladous acetate to form α,β -unsaturated ketones has been reported and explained by oxypalladation and dehydropalladation mechanism.²⁸⁾



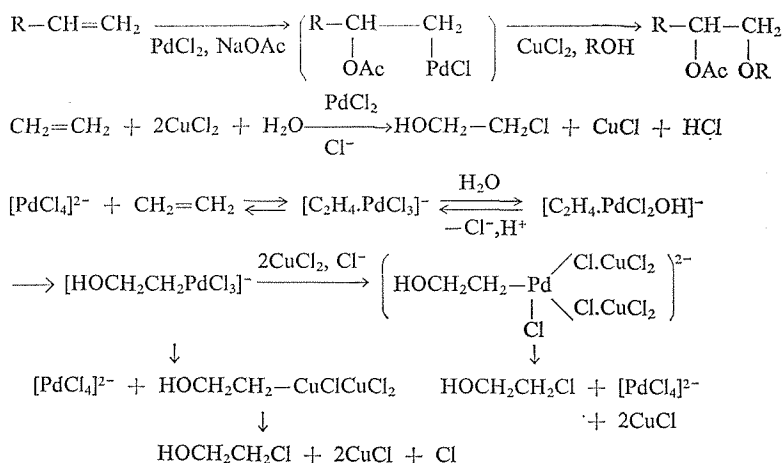
This reaction requires the presence of oxygen. No explanation, however, has been presented.

When chlorine is involved in proper positions of the substrate, no oxidation proceed. Instead, substitution of chlorine proceeds.²⁹⁾



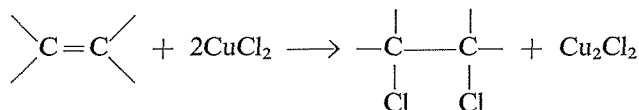
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It is well known that, in palladium salt oxidation of olefin, cupric salt is added to oxidize palladium metal to palladous salt and to make the reaction catalytic. The addition of cupric salt, however, changes the types of product in some cases. In the presence of cupric chloride, saturated compounds are formed, while only unsaturated product are obtained in the absence of the salt.³⁰⁾ The following examples are reported, although the mechanisms are not yet clear.



c. Chlorination of double bond with metal chlorides

Although the formation of π -complex between cuprous salts and olefins is well known, only few examples of those with cupric salt have been reported.³¹⁾ However, the chlorination of olefins with cupric chloride was found to proceed under milder conditions.³²⁾ At least as a transient intermediate, it appears that some complex is formed as an intermediate and subsequent oxidation results in chlorination reaction.



Halogenation with metal halides including the chlorination is reviewed in an article in the next issue.

ACKNOWLEDGMENT

We wish to acknowledge the diligent efforts of many coworkers mentioned in the references.

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